

# **Design and Development of a Highly Sensitive, Field Portable Plasma Source Instrument for On-line Liquid Stream Monitoring and Real-time Sample Analysis**

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The development of a highly sensitive, field portable, low-powered instrument for on-site, real-time liquid waste stream monitoring is described in this paper. A series of factors such as system sensitivity and portability, plasma source, sample introduction, desolvation system, power supply, and the instrument configuration, were carefully considered in the design of the portable instrument. A newly designed, miniature, modified microwave plasma source was selected as the emission source for spectroscopy measurement, and an integrated small spectrometer with a CCD detector was installed for signal processing and detection. An innovative beam collection system with optical fibers was designed and used for emission signal collection. Microwave plasma can be sustained with various gases at relatively low power, and it possesses high detection capabilities for both metal and nonmetal pollutants, making it desirable to use for on-site,

real-time, liquid waste stream monitoring. An effective in-situ sampling system was coupled with a high efficiency desolvation device for direct-sampling liquid samples into the plasma. A portable computer control system is used for data processing. The new, integrated instrument can be easily used for on-site, real-time monitoring in the field. The system possesses a series of advantages, including high sensitivity for metal and nonmetal elements; in-situ sampling; compact structure; low cost; and ease of operation and handling. These advantages will significantly overcome the limitations of previous monitoring techniques and make great contributions to environmental restoration and monitoring.

## **I. INTRODUCTION**

Plasma source spectrometry is a powerful technique for elemental analysis. This technique possesses high sensitivity, good precision, and relatively low backgrounds. Various plasma sources have been developed as excitation/ionization sources for elemental analysis over many years. The technique has been widely used in waste management, industrial hygiene, and environmental sample analysis [1-4]. However, due to lack of compact, inexpensive, and field portable instruments, analysis of samples is typically carried out in the analytical laboratory. Traditional methods for monitoring hazardous elements in liquid waste streams are both labor-intensive and time-consuming. The samples must be collected through sampling vessels and then taken back to the laboratory for off-line analysis by an appropriate spectrometry technique such as atomic absorption, atomic emission, or plasma mass spectrometry. For these applications, typical analytical protocols consisting of sample collection, transportation, and storage procedures will potentially change the true components and chemical structures of the original samples, and the analysis can sometimes give false information. Furthermore, this kind of approach is not applicable to real-time information acquisition and gives out-of-time results. The characteristics of the current off-line instruments exclude them from many industrial and federal applications, such as online, real-time field inspection and monitoring. Since real-time monitoring does provide very critical information for industrial manufacturing facilities, federal agencies, waste management, hazardous waste control, and environmental protection, the need for real-time instrument is obvious. These

recognized needs have stimulated research work to adapt laboratory instruments for field testing and monitoring in order to provide timely results [5-8].

A few analytical techniques have been explored for on-site monitoring of hazardous metals or other pollutants in liquid waste streams. Of these techniques, the most promising methods are inductively coupled plasma (ICP) source atomic emission spectrometry and laser induced breakdown spectroscopy (LIB). In these studies, large commercial ICP atomic emission spectrometers (AES) have been adapted for on-site measurements [5-8]. Since the ICP-AES spectrometers have huge volume, heavy weight, and need over a thousand watts of power and large gas flow rates for plasma generation and maintenance, they are awkward and very hard to use for on-site when high power line and/or argon sources are not readily available. It is difficult to use them for ocean exploration, aircraft testing sites, lake/river contamination surveys, and field-related elemental hazardous monitoring. These difficulties significantly restrict the applications of the technique. Based on these concerns and limitations, there is a clear demand for new instruments and strategies for field portable inspection and/or online, real-time monitoring.

In this work, a new portable instrument for on-site, real-time liquid waste stream monitoring was designed and developed. A series of factors, such as system sensitivity and portability, plasma source, sample introduction device, desolvation system, power supply, and instrument configuration, were carefully considered in the design of the portable instrument. Although an ICP source can provide good sensitivity for elemental

analysis, it is very difficult to integrate an ICP into a small, low cost instrument because of its complex structure and relatively large heavy power system, as well as its high flow rates of supporting gases. Microwave induced plasma (MIP) is a powerful alternative source for elemental determination, and has been extensively used in analytical atomic spectrometry [9-12]. Compared with other types of plasma sources, the MIP offers some attractive characteristics, such as its unique features of high excitation efficiency for metal and nonmetal elements; the capability of working with various gases; simplicity, and low cost for instrumentation and maintenance. Microwave plasmas can be sustained at fairly low power and low gas flow rate, making them a desirable source for on-site, real-time waste stream monitoring.

## **II. INSTRUMENTATION**

### *Instrument assembly and construction*

A sensitive microwave plasma technique was implemented in our portable spectrometer design and development for on-site, real-time monitoring. Figure 1 shows the prototype instrument in its first version, and Figure 2 gives the schematic of the new instrument. In the instrument design, a recently developed microwave plasma device, which is referred to as microwave plasma torch (MPT), was selected as an excitation source for atomic emission spectrometry. Samplings from standard solutions and waste streams can be completed through a peristaltic pump or a flow injection valve. Aerosols can be generated through a nebulizer and can be carried into the plasma by the carrier gas. A hand-size, integrated customer design spectrometer with a CCD detector is used

for optical beam dispersal and detection. To enhance the system performance, a high-efficiency desolvation device was specially designed for the sampling system. A notebook computer with an interface board is used for system control and data processing. Using these components and arrangements, a very compact microwave plasma instrument was constructed and integrated. The instrument can be applied to on-site, real-time waste stream monitoring. The new instrument, compared with ICP-AES, is smaller in size, much lower in power and gas flow rates, and much cheaper to purchase and maintain. This new instrument will provide a handy service for *in-situ* analysis, and eliminate possible sample preparation procedures and errors.

### *Microwave plasma torch and the power system*

The microwave plasma torch is a recently developed microwave plasma generation device [13]. The flame-like plasma formed by the MPT has been demonstrated to be an excellent source for atomic emission spectrometry [13-17], atomic mass spectrometry [18-21], and atomic fluorescence spectrometry [22-23]. MPT discharges show excellent performance with liquid solution sampling and are robust with various samples. The coaxial configuration of three tubes, similar to an ICP, offers some additional advantages over conventional microwave plasma sources [24-27]. Various gases, including argon, helium, nitrogen, and even air, can be used as working gases to generate plasmas. In this new portable instrument, argon and helium are most frequently used for this purpose.

To make the instrument portable, a miniature microwave plasma source was developed based on the original design in the literature [13]. Some significant modifications have been made based on our regular size source to match the needs for the instrument design. First, the torch length was cut. It uses one fourth wavelength in a 2450 MHz power supply instead of the three fourths wavelength torch previously used in our laboratory and the literature [13-17]. Secondly, various materials were tested for the central tube of the torch, including copper, stainless steel, quartz, and ceramic. Stainless steel and ceramic tubes give the best performance, and ceramic tube shows best sample erosion tolerance on the tip of the central tube. In order to prevent microwave leakage and radiation, an attached screen shielding house was designed and built for the miniature torch. The torch is set on an X-Y-Z three-dimensional adjustable stage, which can be used to precisely adjust the plasma position and to facilitate alignment of the beam-collection system. An UV-protected window was installed in front panel of the instrument for observing the plasma performance. The torch is connected to a 2450 MHz microwave power supply through a one-meter 50  $\Omega$  co-axial cable. The maximum output of the power system is 300 W. The microwave energy is transferred to the plasma through an antenna. Plasma can be generated with an initial forward power around 30 W or so, and can be stably operated from 50 W to 300 W. Appropriate adjustment of the torch can minimize the reflected power, which is typically less than 10 W during operation.

### *Optical beam collection and focusing*

Since the microwave plasma used in this work takes a toroidal shape, and the atomic excitation efficiency inside of the plasma is distance-dependant, it is very crucial to set up an efficient beam collection system in the small, portable instrument. In this work, the optical beam collection system for side-on view is assembled with optical fibers and lenses. In the initial design, a collimating lens was installed at one end of the fiber and placed toward the plasma to collect emission beam and focus the beam into the fiber optics. Since the diameter of the collimating lens is only about 5 mm, the solid angle of beam collection is quite small, with an estimated efficiency around 5% or less. With this optical arrangement, the signal magnitude and stability are very sensitive to some operating parameters, such as microwave power and gas flow rates. To solve the problem and increase beam collection efficiency, a double lens focusing assembly was developed to enlarge the beam collection solid angle and to therefore enhance the system sensitivity and signal stability. Significant improvement in system performance was obtained with this new optical lens setup. To further increase the system sensitivity, a cylindrical lens was installed on the detector to increase light collection efficiency. All of these modifications improve the beam collection efficiency and the overall system performance.

### *Integrated spectrometer and data processing*

A customer-designed, integrated, dual-channel spectrometer with two gratings is being used for optical beam dispersal and signal measurement. The major parameters of the spectrometer are listed in Table 1. A Sony ILX511 linear CCD array detector with



2048 element pixels was installed for instantaneous measurements of analyte signals. It sends an analog signal consisting of a stream of voltage levels that are proportional to the light hitting each pixel on the detector element. The spectrometer has a small well depth. It can be used to record signal intensity up to as much as 4000 counts. The wavelength range from about 200 to 480 nm is covered by the two channels of the spectrometer. Although different groove gratings and different diameter fiber optics were tested during the system evaluation, 200-micron diameter fibers and 2400 grooves/mm gratings were most frequently used for spectral measurements.

An OOIBAS 32-bit software package was used for all data acquisition and control. This software has an advanced acquisition and display program that provides a real-time interface to the signal-processing function. A notebook computer with a 100 kHz sampling frequency DAQ-700 card is used to show real time spectrum on its screen and store data. A CBL-2-NI interface cable is used to make a connection between the spectrometer and the computer.

### *Sample introduction and desolvation*

Solution samples and/or waste streams can be delivered through a commercial peristaltic pump into an ultrasonic nebulizer (U-5000 AT, CETAC Technologies INC.), where the liquid samples are generated into fine, wet aerosols through an ultrasonic transducer. The heating temperature inside the ultrasonic nebulizer is 140° C, with a cooling chiller operating to -5 °C at the aerosol outlet. The aerosol generation efficiency

by the system is around 10% with a sample uptake rate of 0.75 ml/min. To further control the solvent loading in the low power plasma and enhance the system sensitivity, an additional high efficiency desolvation device was designed and built specifically for our new instrument. This self-assembled desolvation device includes a two-step desolvation process. A membrane desolvator, with a stainless steel chamber, is used for the first stage. A nitrogen gas stream of about  $0.5 \text{ L min}^{-1}$  flow rate was introduced into the space between the stainless steel chamber and the membrane tube to remove the water vapor produced during the desolvation process. To increase the membrane desolvation efficiency, a heating tape was placed at the entrance of the tubing to warm up the aerosols. At the tubing exit, a sieve sorbent device was applied to further absorb the residue water vapor. With this arrangement, comparative desolvation efficiency was obtained using this new system and using the old system discussed in the literature [28]. However, the new system seems much easier to handle and can be integrated into the portable instrument.

### III. SPECTRAL MEASUREMENTS

#### *Spectrum acquisition modes*

Background emissions from an argon plasma were well characterized at the initial step of the instrument testing. The major contributions to the background emission in UV range are NO, OH, and NH molecular emission bands. The intensities of these molecular bands vary with the observation region on the plasma. In most cases, as shown

in Figure 3 (a), OH and NH are the dominant bands in the background emission. It seems that there is no significant difference between the background emissions whether or not a blank solution is used, which is believed to be due to the high efficiency of the desolvation.

Two spectrum acquisition modes, with and without background contribution, were tested during the instrument operation. A typical spectrum from either of the data collection modes is given in Figure 3. Figure 3 (a) shows the background spectrum with a blank solution, and Figure 3 (b) gives the spectrum with a 10 ng/ml beryllium solution introduced. Subtracting (a) from (b) gives Figure 3 (c), which represents a “pure” contribution from the sample solution without significant background contribution. This background-subtraction process can be done and stored with the computer software used in the spectrometer, and therefore, a real-time display for a “pure” sample spectrum can be generated at any time based on the operator’s requirement. In this way, the background influence from molecular bands on an analyte’s spectral lines can be significantly suppressed or even completely eliminated. Obviously, this background subtraction mode can enhance the system’s sensitivity, especially for the elements with spectral lines falling on these molecular background bands.

It should be noted that the both optical resolution of the spectrometer and the data collection step-width determined by computer software have significant influence on the performance of the background subtraction. At the initial step, a 1200 grooves/mm grating was used with a data collecting step-width of about 0.14 to 0.19 nm, depending

on the wavelength. The results obtained from a 100 ng/ml beryllium solution are shown in Figure 4. Figure 4 (a), (b), and (c) show the background, signals with background, and signals without background, respectively. Obviously, the background subtraction in Figure 4 (c) is much worse than the spectrum obtained in Figure 3 (c), and mismatching from point to point can be observed due to the lower resolution grating and the wider step-width used by the computer software. The new portable instrument currently uses a 2400 grooves/mm grating and a data collection step-width of about 0.08 nm. The typical results obtained with this updated system are as shown in Figure 3.

### *Fiber optics*

The influence of the diameter of fiber optics on analytical performance was examined from 200 to 1000-micron. A slight increase in “pure” signal intensity was observed when we switched fiber optics from 200 to 600 micron, and a decrease in net signal was obvious when a 1000 micron fiber was used (Figure 5). Background examinations show that all the molecular bands increased significantly with an increase in the fiber diameter. Considering that the CCD detector used in this instrument has very limited maximum counts around 4000 and is easily saturated, in most cases, 200 and 300-micron fibers are best used with the instrument.

### *Resolution*

Optical resolution of the instrument is based on the groove density of the grating and the diameter of the entrance optics or slit. Several other factors, such as the diameter of the fiber optics and the data acquisition step-width, may also influence the resolution. Usually, there is a trade-off between optical resolution, signal intensity, and spectral range, because only a very small grating is used in each channel of the spectrometer. In the current system, the entrance slit is fixed at 10  $\mu\text{m}$  with 1-mm height in order to get better resolution. Several gratings from 1200 grooves/mm to 2400 grooves/mm were tested during the instrument characterization. The lower groove grating (1200 grooves/mm) can give wider spectral range but have poor resolution (around 0.5 – 0.6 nm). The best optical resolution of about 0.3 nm can be achieved with 2400 grooves/mm grating and about 150 nm spectral range.

### *Spectra with the new instrument*

Several elements have been examined with the newly developed portable instrument. Figure 6 gives a typical spectrum obtained with multiple elements at solution concentration from 100 ng/ml to 1  $\mu\text{g/ml}$  and an integration time of 50 ms. Other experimental conditions can be found in the figure caption unless otherwise stated. Figure 7 shows the spectrum obtained from tap water with five times dilution at wavelength range from 200 to 350nm, which is the master channel coverage of the spectrometer. Strong peaks from magnesium spectral lines at 285.2 nm and 279.6/280.3 nm can be observed from the spectrum. However, integration of each peak from the spectrum has not been desperately pursued at this work.

#### **IV. ANALYTICAL FIGURES OF MERIT**

Based on the above preliminary examinations, the portable spectrometer's detection limits for Ag, Be, Cd, Cu, Hg, Mg, Mn, and Zn range from 9 pg/ml to 0.77 ng/ml, depending on the individual elements and the spectral line used. Table 2 lists detection limits for each individual element. These values are comparable or superior to the best values reported with current huge bench-top AES instruments [1-2,12,29]. The relative standard deviation (RSD) of the new instrument has also been evaluated with short-term measurements. The estimated RSD values are in a range from 1.8 to 3.5%, based on 21 measurements. Both detection limits and RSD can be further improved simply by using longer integration time. However, a longer integration time may restrict real-time function of the instrument.

#### **V. DISCUSSION**

A field portable instrument combined with a microwave plasma source for on-site, real-time waste stream monitoring has been successfully developed. An effective in-situ sampling system coupled with a high efficiency desolvation device has been designed for direct liquid solution sampling. The new instrument can be easily used for field inspection, provides handy service, and timely information for on-site, real-time monitoring. The new instrument possesses a series of advantages, including high sensitivity for most elements; in-situ sampling; compact structure; low cost; and easy

handling. These advantages overcome some of the limitations of previously used monitoring techniques and make great contributions to environmental restoration and monitoring.

## ACKNOWLEDGMENTS

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**Table 1. Parameters of the spectrometer**

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Model	Customer SD2000
Channel	2
Spectral range	200 – 480 nm
Grating	2400 grooves/mm
Slit	Fixed at 10 $\mu\text{m}$
Pixel resolution	3.2 pixels
Blaze wavelength	holographic/UV
Detector	Sony ILX511 CCD linear arrays 2048 elements, well depth, 350,000 photons
Optical resolution	0.3 nm
Fiber optics	200 $\mu\text{m}$ x 2 m

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Table 2. Detection limits obtained with the new portable instrument

<b>Element</b>	<b>Wavelength (nm)</b>	<b>Detection limits (ng/ml)</b>
Ag (I)	328.1	0.21
Ba (I)	455.5	0.24
Be (II)	313.1	0.009
(I)	234.9	0.047
Cd (I)	228.8	0.41
Cr (I)	425.4	0.22
Cu (I)	324.7	0.13
Hg (I)	253.7	0.44
Mg (I)	285.2	0.078
Mn (II)	257.6	0.77
(I)	279.5/279.8	0.76
Zn (I)	213.8	0.39

## Figure captions

Fig. 1: prototype portable instrument

Fig. 2: Schematic diagram of the instrument assembly

Fig. 3: A typical spectrum with and without background subtraction using 2400 grooves/mm grating. (a). background spectrum with 1% nitric acid; (b). a 10 ng/ml beryllium spectrum with background; (c). a 10 ng/ml beryllium spectrum with background subtraction. See text for details.

Fig. 4: A typical spectrum with and without background subtraction using 1200 grooves/mm grating. (a). background spectrum with 1% nitric acid; (b). a 100 ng/ml beryllium spectrum with background; (c). a 100 ng/ml beryllium spectrum with background subtraction. See text for details.

Fig. 5: Spectra obtained with different diameter optical fibers. (a). 200  $\mu\text{m}$ ; (b). 600  $\mu\text{m}$ ; (c). 1000  $\mu\text{m}$ .

Fig. 6: A typical spectrum with multiple elements. Concentrations used: 1  $\mu\text{g/ml}$  for Cd, Hg, Mn, Zn, and 100 ng/ml for Cu and Ag.

Fig. 7: Spectrum obtained with tap water sample after five times dilution with deionized water.

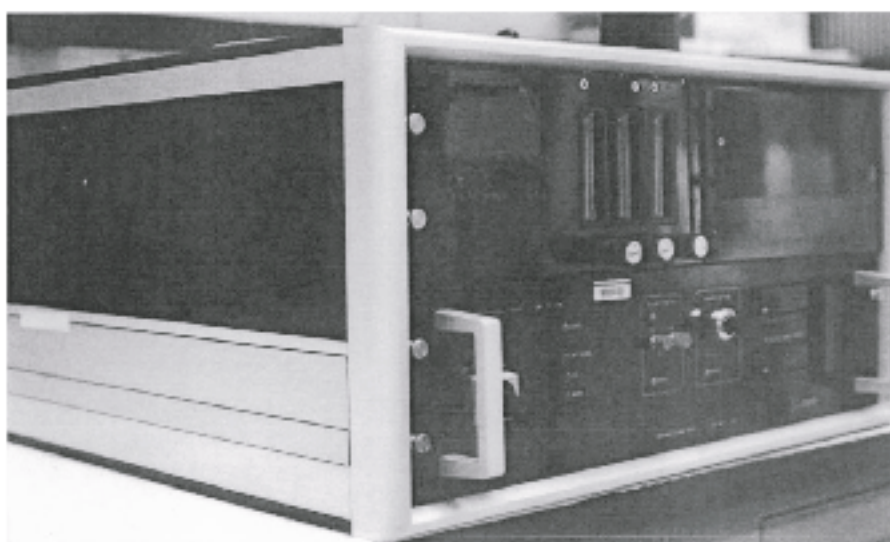
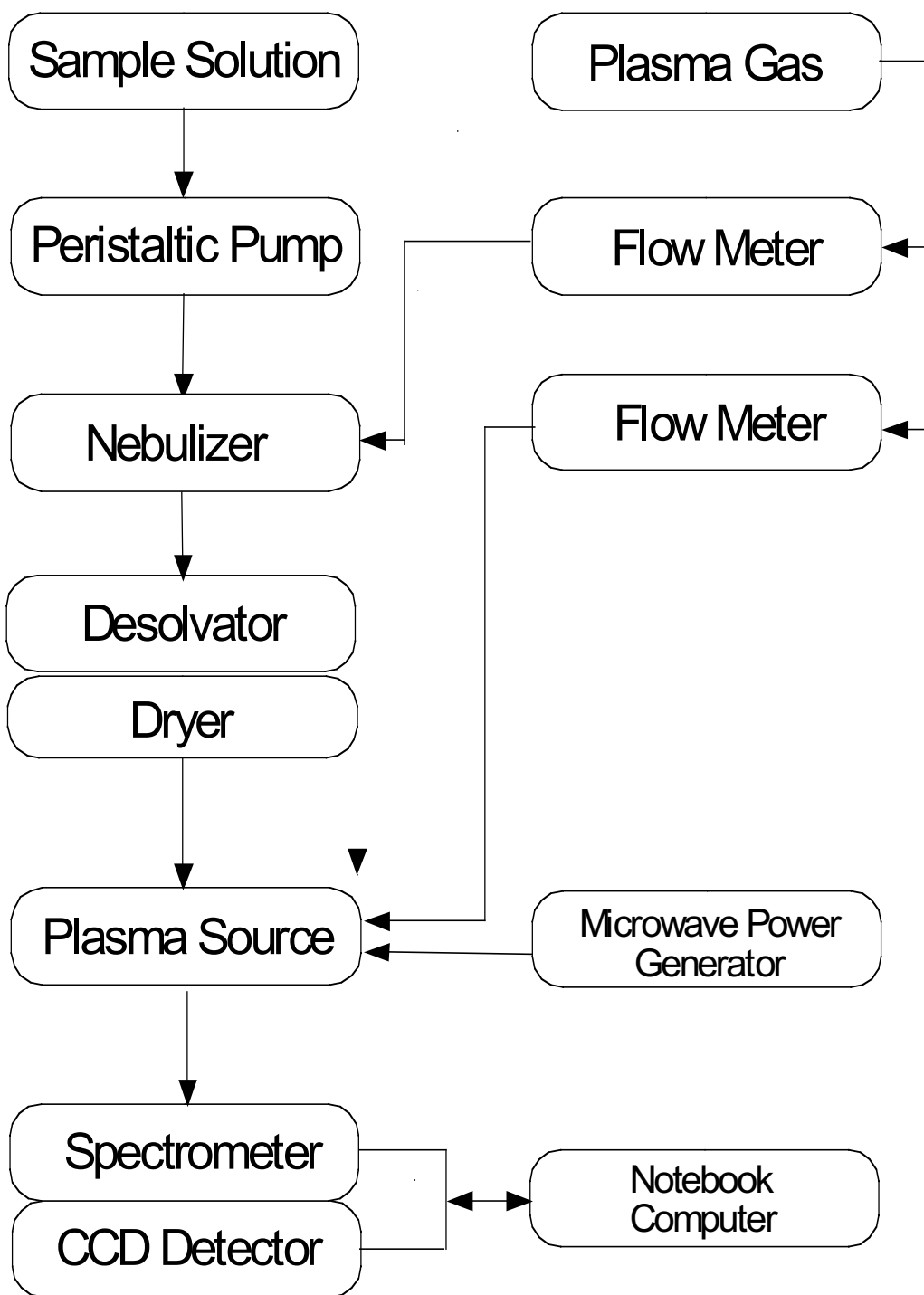
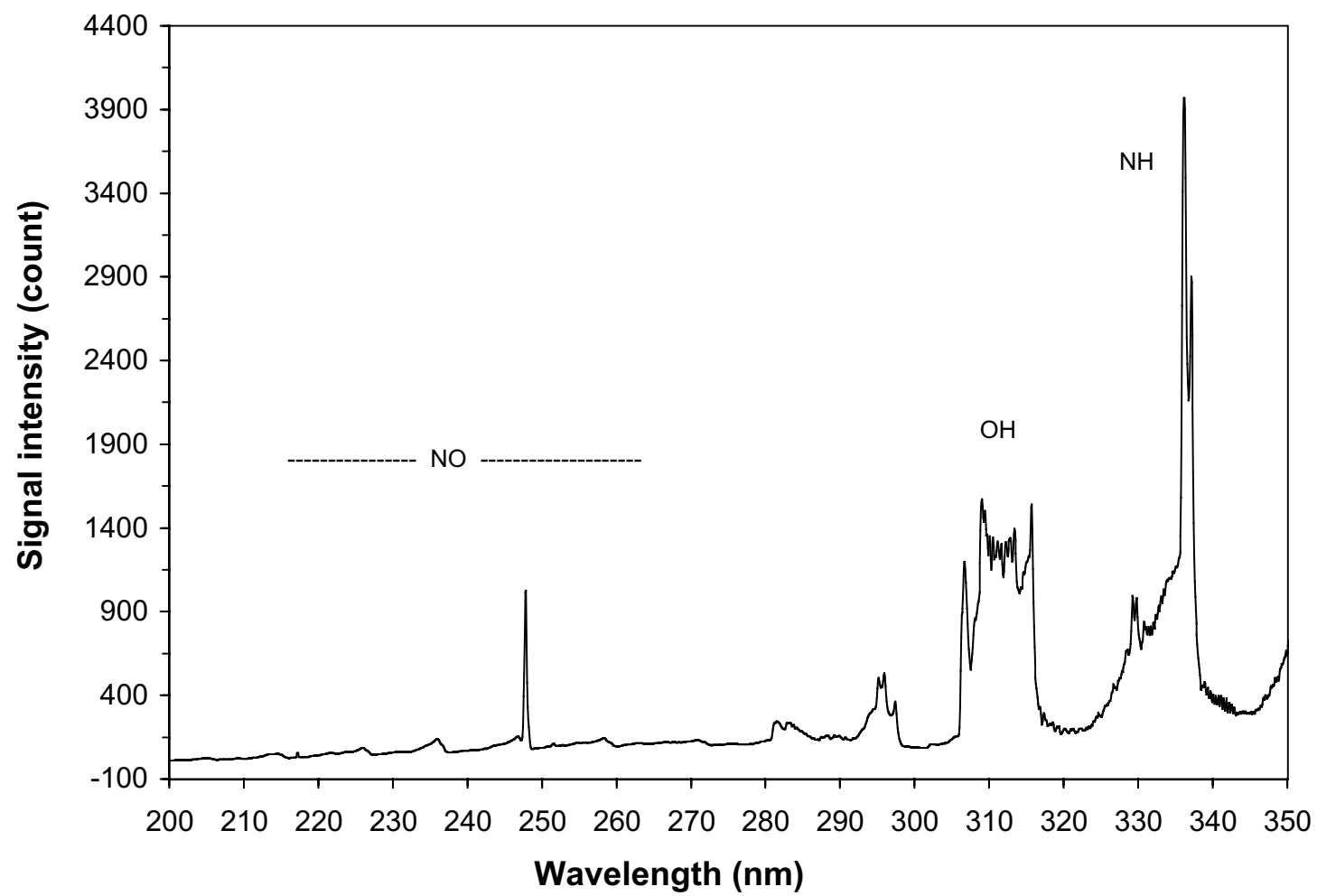
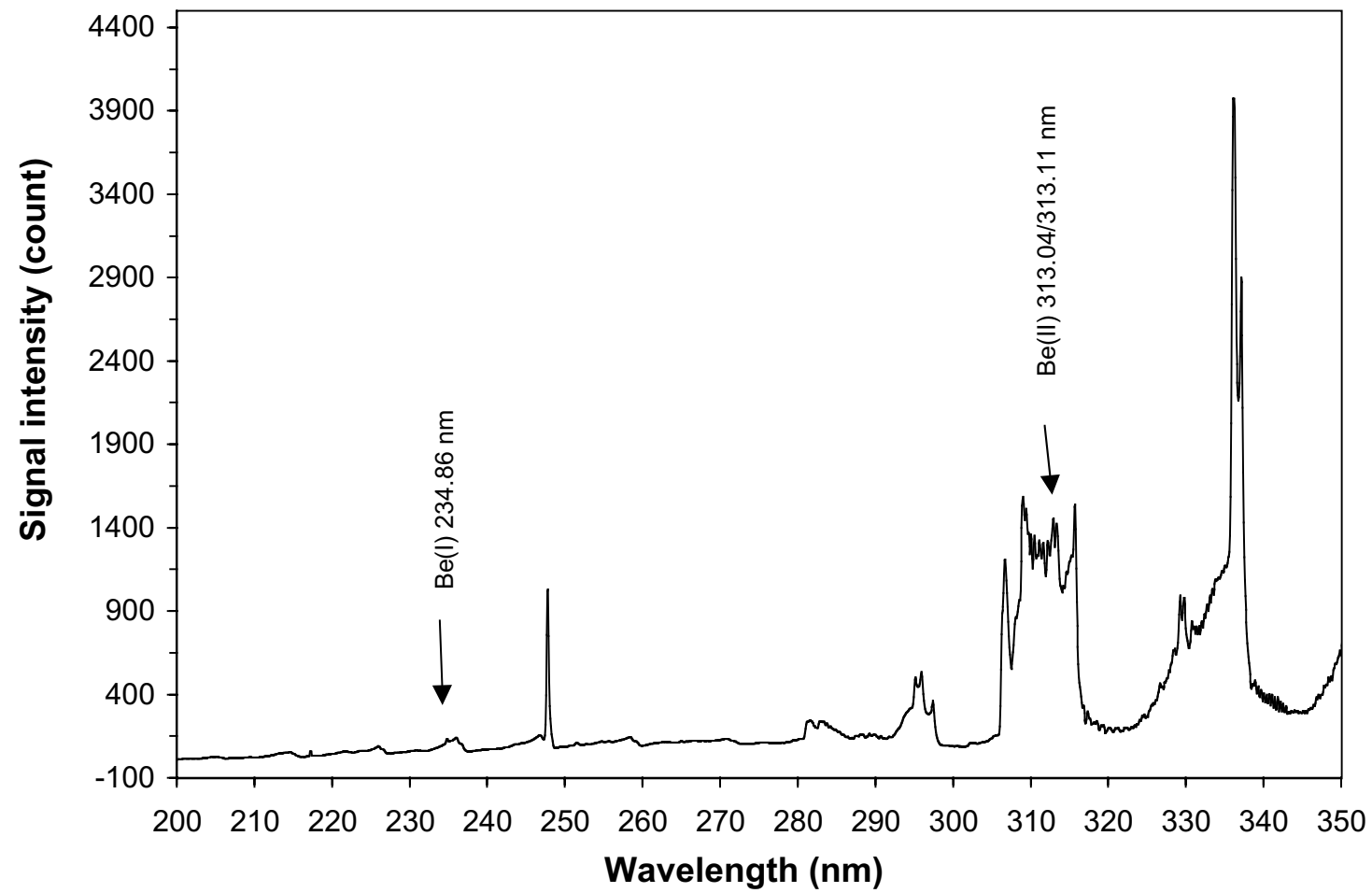
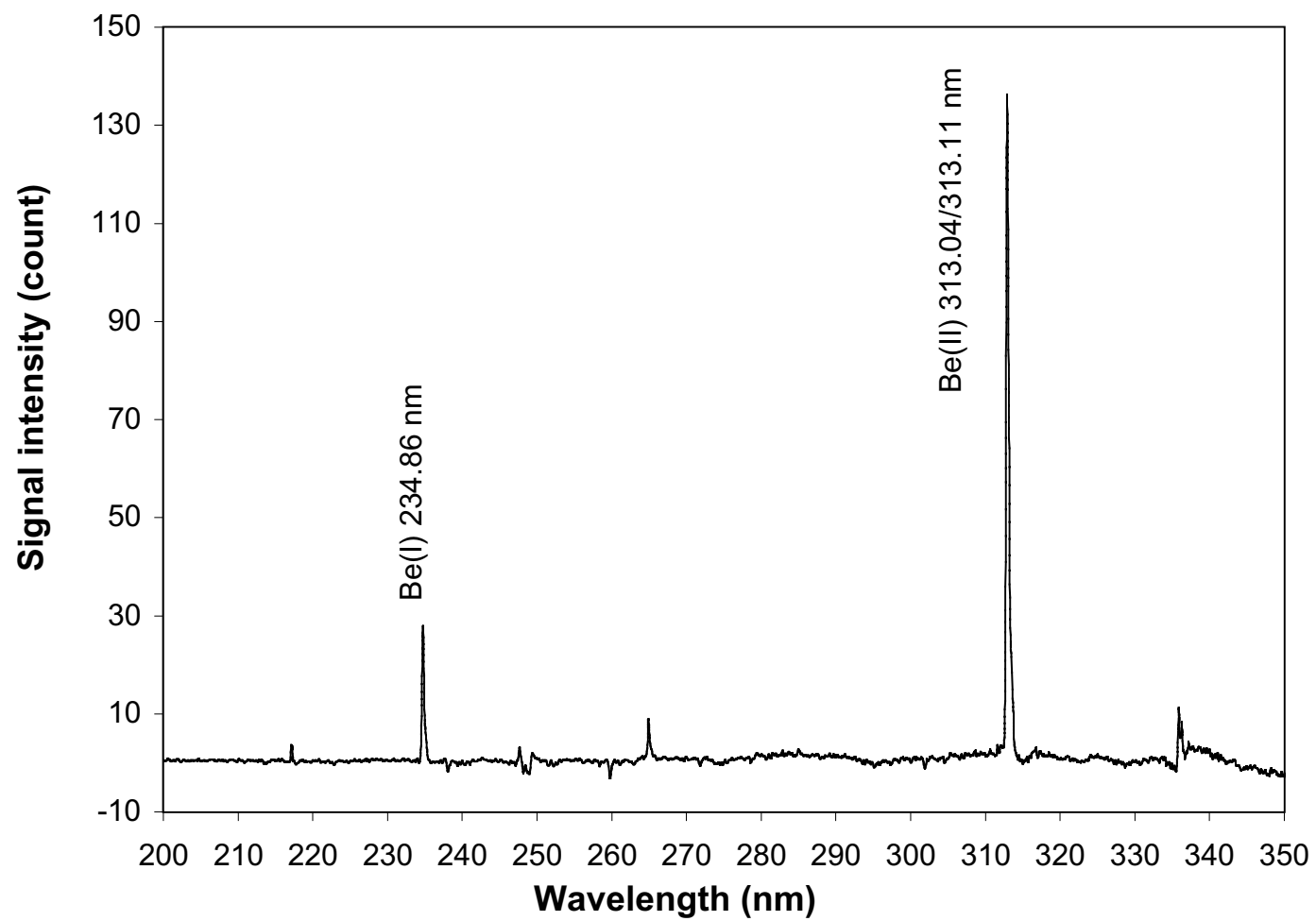


FIG. 1. Prototype portable instrument.

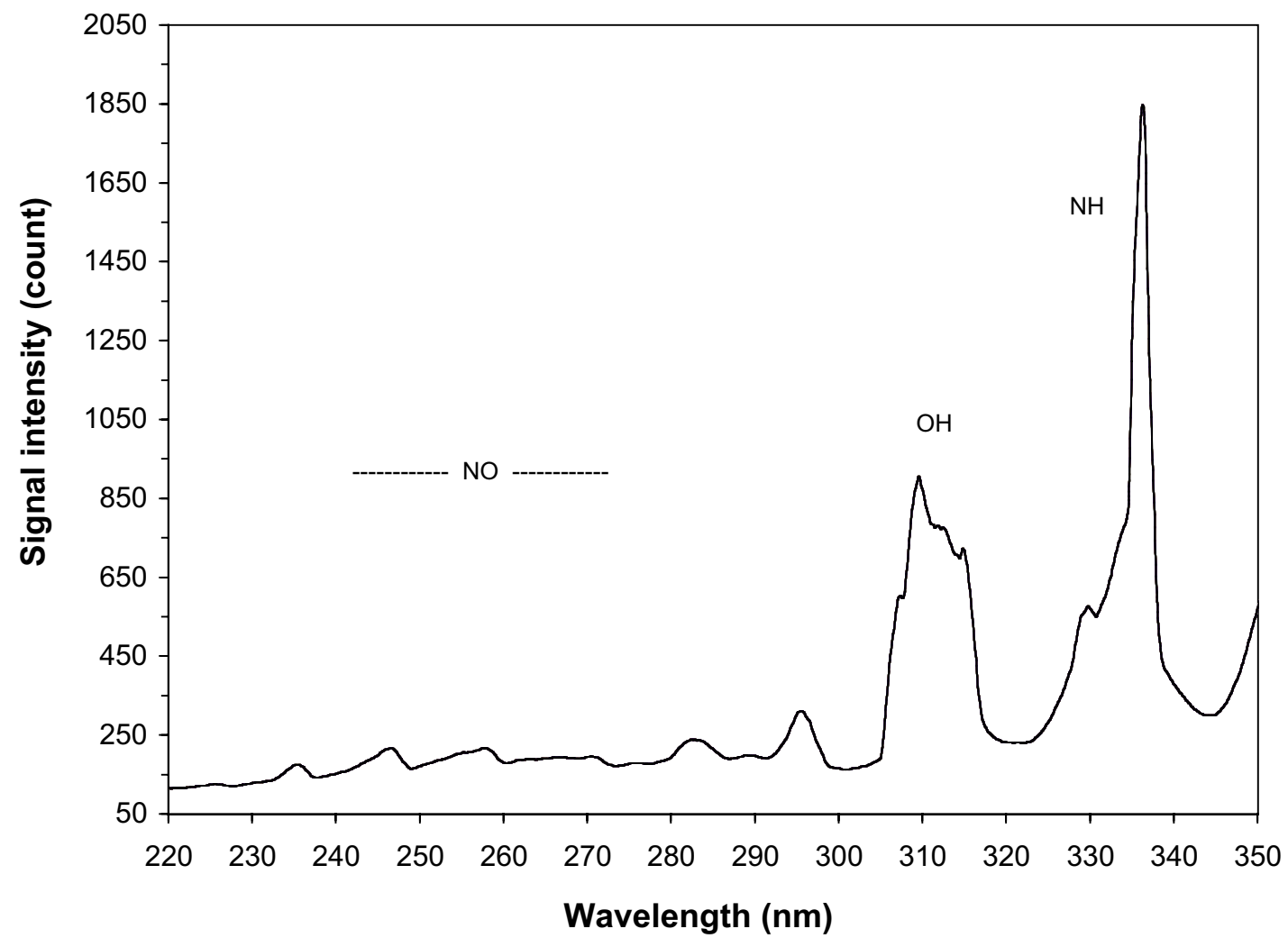


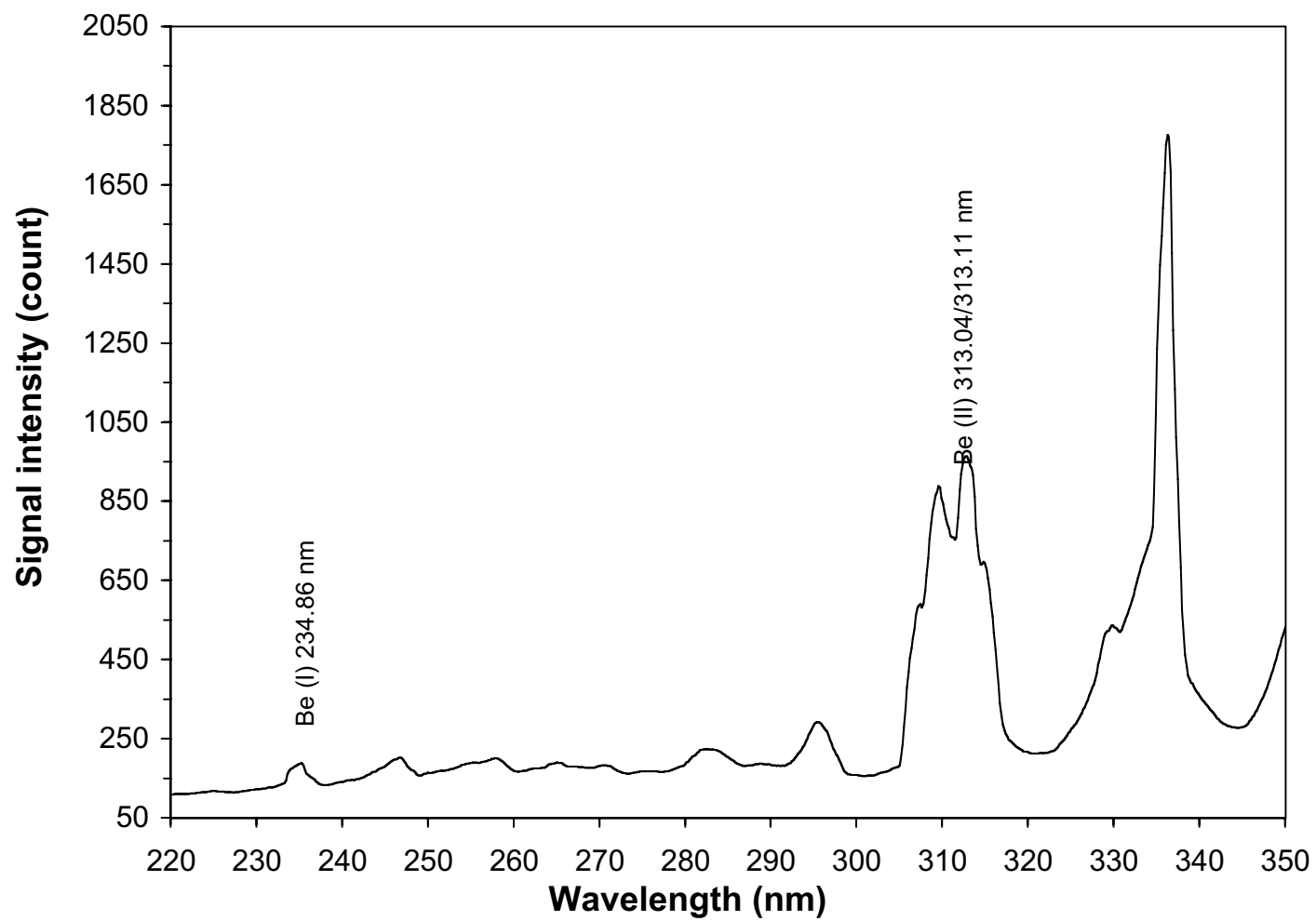


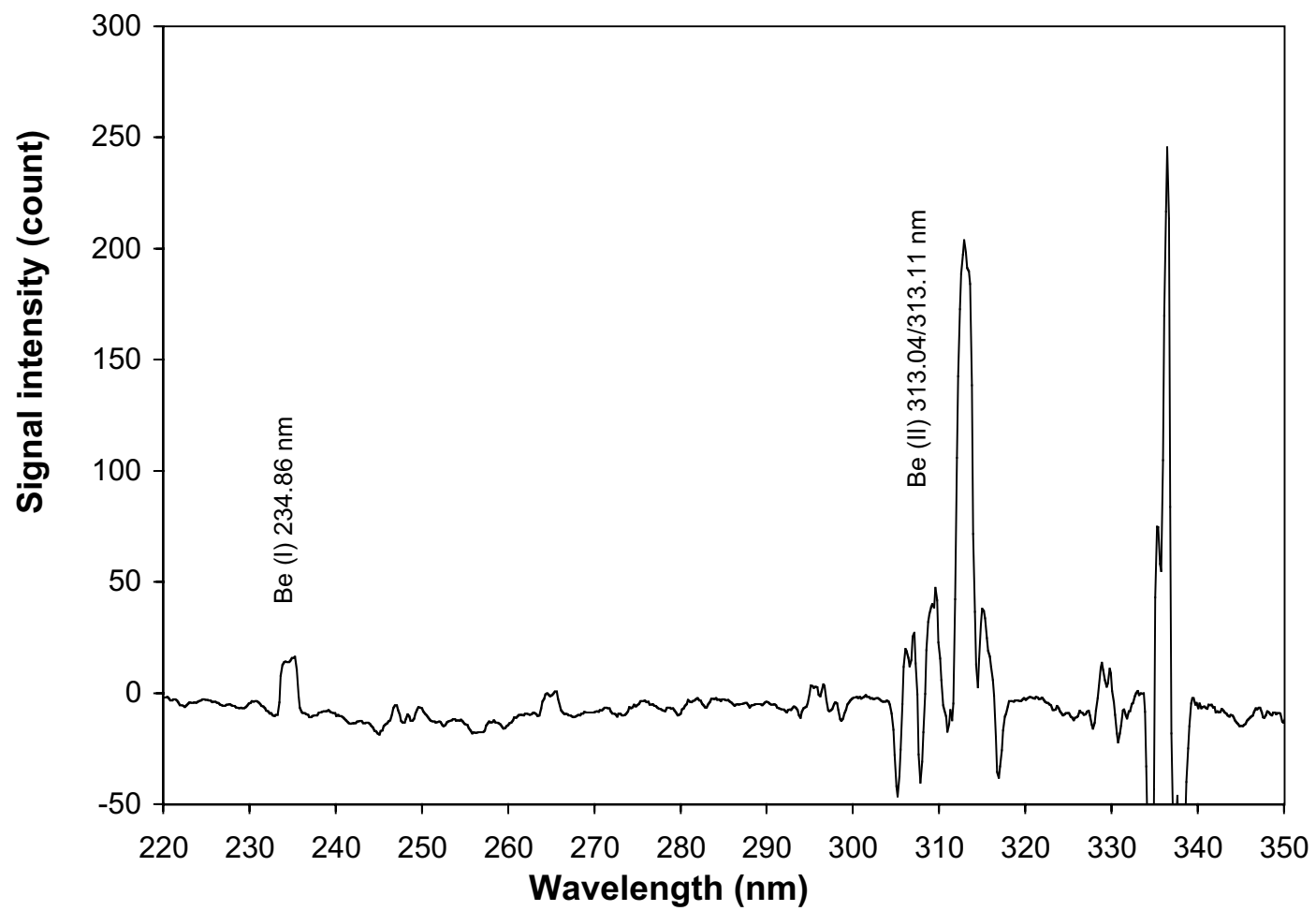












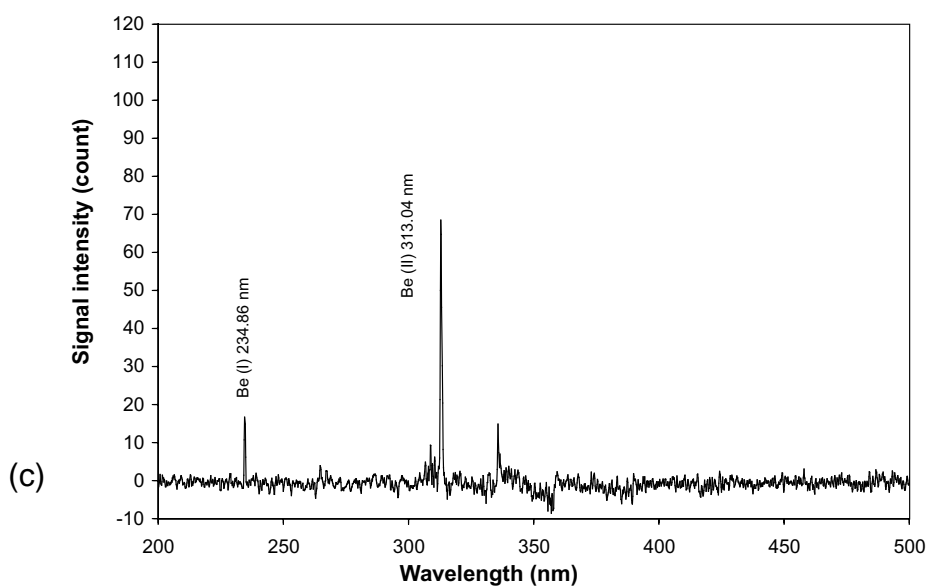
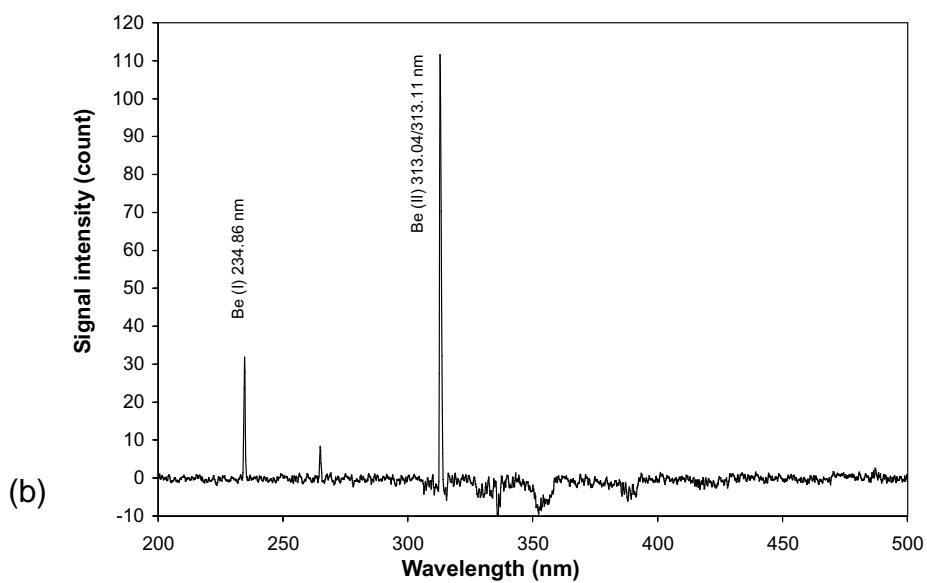
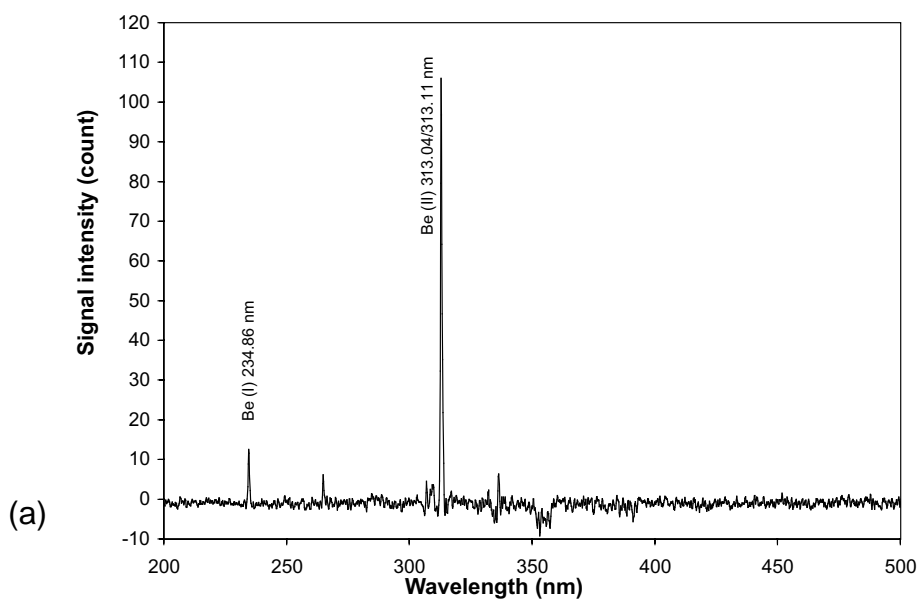


figure 5

